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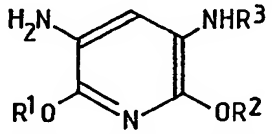
(54) Medium and process for the dyeing of hair

(57) Medium and process for the oxidative dyeing of hair based on a developer substance-coupler substance combination, in which as coupler substance there is used at least one 3,5-diaminopyridine derivative of the general formula



(I)

in which R^1 and R^2 independently mean CH_3, C_2H_5, or C_2H_4OH and R^3 represents hydrogen, C_1—C_4 alkyl or C_1—C_4 hydroxyalkyl, and may be in the form of physiologically-acceptable salts. The preferred substance is 3,5-diamino-2,6-dimethoxypyridine.

The coupler substances according to formula (I) are stable on storage, readily soluble in water and have favourable toxicological as well as dermatological properties. The coupler substances according to Formula (I) provide, in combination with 1,4-diaminobenzene or its derivatives, very intensive blue-black tones without red shading and in combination with 4-aminophenol, very shiny gold-orange tones.

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This print takes account of replacement documents later filed to enable the application to comply with the formal requirements of the Patents Rules 1982.

SPECIFICATION

Media and Processes for the Colouring of Hair

The field of the invention is media and processes for the oxidative colouring of hair, based on developer and coupler substances, in which a derivative of 3,5-diaminopyridine is used as the coupler substance.

Oxidative dyes have attained substantial significance in the colouring of hair. The colouring results in this case from the reaction of particular developer substances with particular coupler substances in the presence of a suitable oxidative medium.

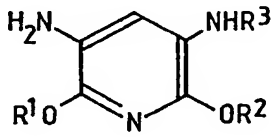
As developer substances 2,5-diaminotoluene, 4-aminophenol and 1,4-diaminoanisol are favoured; however 2,5-diamino-anisol, 2,5-diaminobenzyl alcohol and 2-(β-hydroxyethyl)-1,4-diaminobenzene have also attained a certain significance. In particular cases tetraminopyrimidine can also be employed as the developer substance. The coupler substances that are preferably used are α-naphthol, resorcinol, 4-chlor-resorcinol, m-aminophenol, 5-amino-o-cresol, and derivatives of m-phenylenediamine such as 2,4-diaminophenetol and 2,4-diaminoanisole. These derivatives, as well as m-phenylenediamine itself have in this context, because of their ability during oxidative coupling with 1,4-diaminobenzene or 1,4-diaminobenzene derivatives to generate a blue tone, achieved significance as so-called blue couplers.

Oxidative dyes, which are used for the colouring of human hair, are subject to numerous requirements. Thus they must be beyond question from the toxicological and dermatological point of view and must make it possible to attain colours of the desired intensity. It is further required that by combination of suitable developer and coupler substances a broad range of subtly differing shades can be achieved. Otherwise the attainable hair colours must have a good resistance to light, permanent waving, acids, and abrasion. In all cases must such hair colours remain stable, without being affected by light, chemical media, and abrasion, for a period of at least 4 to 6 weeks.

m-Phenylenediamine, which is used at the present time as a blue coupler, and its derivatives 2,4-diaminotoluene and 2,4-diaminoanisole, as well as the more-recently recommended blue couplers, such as for example 1-hydroxy-3-amino-6-chlorbenzene and 2,4-diaminophenoxyethanol, cannot however satisfactory fulfill the above-mentioned requirements.

The objective of the invention is, therefore, to make available a hair colouring medium as well as a hair colouring process, by means of which the said requirements are better fulfilled.

To this end it has now been found, that media for the oxidative colouring of hair based on a developer substance/coupler substance combination, as well as optionally other conventional colouring components and additives, characterised in that they contain at least one 3,5-diaminopyridine derivative of the general formula I



where R^1 and R^2 independently mean CH_3, C_2H_5 or C_2H_4OH, and R^3 represents hydrogen, C_1 to C_4 alkyl or C_1 to C_4 hydroxyalkyl, possibly in the form of physiologically-acceptable salts, will excellently fulfill the above-mentioned requirements.

The 3,5-diaminopyridine derivatives of Formula I given above, which are contained in the hair colouring media according to the invention as coupler substances, such as for example 3,5-diamino-2,6-dimethoxypyridine, 3,5-diamino-2,6-diethoxypyridine and 3,5-diamino-2,6-di-(β-hydroxyethyloxy)-pyridine, are readily soluble in water. They also display excellent stability during storage, especially as a component of the hair colouring media described herein.

The coupler substances according to the invention of which 3,5-diamino-2,6-dimethoxypyridine is preferred, are to be present in the hair colouring media in a concentration from about 0.01 to 3.0 weight %, preferably 0.1 to 2.0 weight %.

Furthermore, the hair colouring media may additionally contain known coupler substances, especially resorcinol, 4-chlorresorcinol, 2-methylresorcinol, 2-amino-4-(β-hydroxy-ethylamino)-anisol, 2,4-diaminophenylethanol, 2,4-diaminophenoxyethanol, 1,5-dihydroxytetralin, m-aminophenol, 3-amino-2-methylphenol, 3-amino-6-methylphenol, 4-hydroxy-1,2-methylendioxybenzene, 4-amino-1,2-methylendioxybenzene, 2,4-diaminoanisol and 2,4-diaminophenetol.

Of the known developer substances, 1,4-diaminobenzene, 2,5-diaminotoluene, 2,5-diaminoanisol, 2,5-diaminobenzyl alcohol, 3-methyl-4-aminophenol and 4-aminophenol above all come into consideration as components of the hair colouring media.

The above-mentioned coupler and developer substances may be present in the hair colouring media either singly or mixed with one another.

The total amount of the developer substance/coupler substance concentration in the hair

colouring media described herein should amount to about 0.1 to 5 weight percent, preferably 0.5 to 3.0 weight %.

The developer components are used in general in roughly equimolar amounts, with respect to the coupler components. There is however no disadvantage if the developer components are in this respect used in a larger or smaller proportion than equimolar. In particular in order to attain pale shades, it can sometimes be effective to use a smaller than equimolar amount of developer components.

Furthermore, the hair colouring material of this application can additionally contain other colouring components, for example 6-amino-2-methylphenol, 6-amino-3-methylphenol and 6-amino-3-ethoxyphenol, as well as further conventional direct dyes, for example triphenylmethane dyes such as Diamond Fuchsin (C.I. 42 510) and Leather Ruby HF (C.I. 42 520), aromatic nitro dyes such as 2-nitro-1, 4-diaminobenzene, 2-amino-4-nitrophenol and 2-amino-5-nitrophenol, Azo dyes such as Acid Brown 4 (C.I. 14 805) and Acid Blue 135 (C.I. 13 385), Anthraquinone dyes such as Disperse Red 15 (C.I. 60 710) and Disperse Violet 1 (C.I. 61 100), also 1,4,5,8-tetraaminoanthraquinone and 1,4-diaminoanthraquinone.

The coupler and developer substances, as well as other colouring components, can of course, where they are bases, be used in the form of physiologically-acceptable acid addition salts, for example as the hydrochloride or the sulphate or, if they possess aromatic OH-groups-in the form of salts with bases, for example as alkali phenolates.

Still further conventional cosmetic additives can also be used in the hair colouring media, for example antioxidants such as ascorbic acid or sodium sulphite, perfume oils, complexing agents, wetting agents, emulsifiers, thickeners, care media, and others.

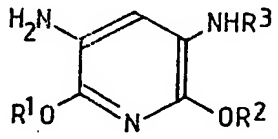
The form of the preparation can be for example a solution, especially an aqueous or water-alcohol solution. The especially-preferred types of preparation are however a cream, gel or emulsion.

Their combination represents a mixture of colouring components with the additives conventional for such preparations.

Conventional additives in solutions, creams, emulsions, or gels are for example solvents such as water, lower aliphatic alcohols, for example ethanol, propanol and isopropanol, or glycols such as glycerol and glycolethers such as propylene glycol, furthermore wetting agents or emulsifiers from the class of anionic, cationic, amphoteric, or non-ionic surface active agents such as fatty alcohol sulphates, alkylsulfonates, alkylbenzenesulfonates, alkyltrimethylammonium salts, alkylbetains, oxyethylated fatty alcohols, oxyethylated nonylphenols, fatty acid alkanoiamides, oxyethylated fatty acid esters, furthermore thickeners such as higher fatty alcohols, starches, cellulose derivatives, vaseline, paraffin oils and fatty acids as used as care materials such as lanolin derivatives, cholesterol, pantothenic acid and betain. These components are used in the conventional amounts for such purposes, for example the wetting agents and emulsifiers can be present in the preparation in concentrations from about 0.5 to 30 weight percent, whilst the thickener can be used in an amount from about 0.1 to 25 weight percent.

Depending on the combination, the hair colouring materials according to the invention can be weakly acid, neutral, or alkaline reacting. In particular, they display a pH value in the alkaline region between 8.0 and 11.5, in which case the composition is preferably prepared with ammonia. However organic amines, for example monoethanolamine and triethanolamine or inorganic bases such as sodium hydroxide and potassium hydroxide, can also be used.

In the process according to the invention for the oxidative colouring of hair, the hair colouring materials are mixed shortly before use on the basis of a developer substance/coupler substance combination including optionally other conventional colouring components and conventional additives characterised in that they contain as a coupler substance at least one 3,5-diaminopyridine derivative of the general formula I



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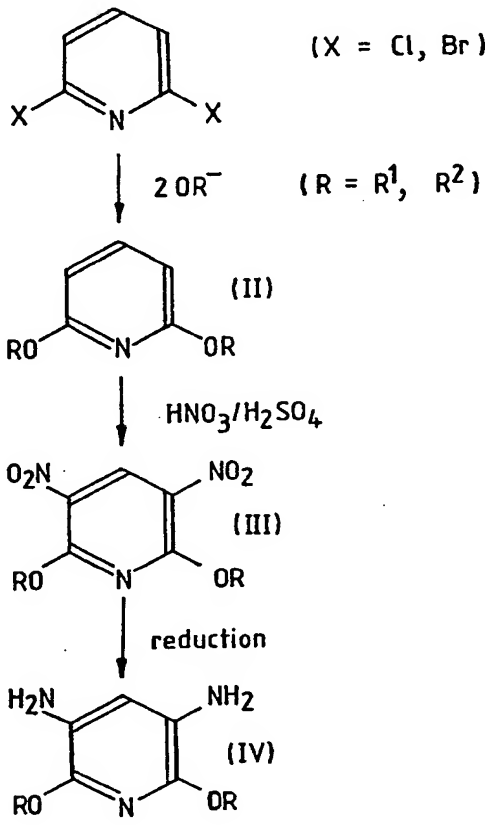
Wherein R^1 and R^2 mean independently CH_3, C_2H_5, or C_2H_4OH and R^3 represents hydrogen, C_1 to C_4 alkyl, or C_1 to C_4 hydroxyalkyl, which may also be in salt form, with an oxidative medium, and this mixture is applied to the hair. As the oxidative medium for the development of the hair colouring, hydrogen peroxide, for example as a 6% aqueous solution or as an addition compound with urea, melamine or sodium borate, comes mainly into consideration. The mixture is allowed to act on the hair at 15 to 50°C for about 10 to 45 minutes, preferably 30 minutes, the hair is then rinsed and dried. If desired the hair can, in connection with this rinsing, be washed with a shampoo and possibly re-rinsed with a weak organic acid, such as citric or tartaric acid. Finally the hair is dried.

The preparation of the 3,5-diaminopyridine derivative contained in the hair colouring media described herein is known. Relevant information can for example be obtained from German laid-open specification 2445002. By a further synthetic route, 2,6-dichloro- or 2,6-dibromo-pyridine is employed

as starting material. According to the following reaction scheme, by nucleophilic substitution of the halogen with the corresponding alkoxide and finally by nitration, the corresponding 3,5-dinitro-2,6-dialkoxypyridine (III) is arrived at. Finally, the thus-obtained dinitro compound is converted to the desired 3,5-diamino-2,6-dialkoxyl compound (IV) by reduction of the nitro groups.



The corresponding N-substituted derivatives of 3,5-diamino-2,6-dialkoxypyridine are also attainable by common synthetic steps which are described in the chemical literature. Thus the 2,6-dialkoxypyridine compound (II) is next mononitrated, and finally the nitro group is reduced to an amino group. The monoalkylation of the amine nitrogen follows. The end product is obtained by a further nitration and a following reduction of the nitro group to an amino group.

From the viewpoint of the colour possibilities, the hair colouring media according to the invention offer, depending on the type and combination of the colouring components, a broad palette of various subtle shades, which range from blondes via browns, ash tones, pale tones, golds to blue and black tones. In this connection the shades show particular colour intensity and resistance to light.

The progress attained from the dermatological and toxological viewpoint by the use of the 3,5-diaminopyridine derivative of the formula (I) given therein in the hair colouring media described herein, for example in comparison to the known blue couplers 2,4-diaminotoluene, 2,4-diaminoanisol, and m-phenylenediamine, is of particular significance. Thus the coupler substance according to the invention 3,5-diamino-2,6-dimethoxypyridine, shows in the Ames test, and in contrast to 2,4-diaminotoluene or 2,4-diaminoethylbenzene, no mutational effect on salmonella-typhimurium stock.

The above mentioned pyridine derivatives give as coupler substances in combination with the developer substances 1,4-diaminobenzene and its derivatives very intense blue-black tones without any red component, which cannot be attained with the known coupler substances for use in hair colouring media, such as for example 2,4-diaminotoluene, 2,4-diaminoanisol, 2,4-diaminophenoxyethanol, 2,6-diaminotoluene, 2-amino-4-(β-hydroxy-ethyl-amino)-anisol or 3-amino-6-chlorphenol.

With the blue couplers that are required for the generation of pale and ash tones with the 1,4-diamino components mentioned above as developer substances, there is also given a red- or violet-tinged blue tone, so that the attainment of pale and ash tones becomes impossible or very difficult. In contrast to this, because of the advantageous properties of the pyridine derivatives according to the invention, it is now possible without problems to achieve blue tones without a red tinge, to dye the hair

in long-lasting natural ash or pale tones, which also remain stable towards light and do not, like the shades produced using m-phenylenediamine, fade to red.

A further advantage of the 3,5-diaminopyridine derivatives contained in the hair colouring media according to the invention consists in the broad spectrum of colour tones that can be produced. So for example, in combination with 4-aminophenol as developer substance, very shiny fashionable gold-orange tones may be created, for the production of which it was until now necessary to use mixtures of various couplers.

Finally, with the help of the hair colouring media according to the invention, it is also possible to dye grey hair which has not been chemically damaged without problems and with very good covering power.

The following Examples are to more closely describe the subject-matter of the invention.

Examples

Example 1—Hair colouring medium in gel form.

0.75 g.	3,5-diamino-2,6-dimethoxypyridine-dihydrochloride,
0.70 g.	2,5-diaminotoluene sulphate,
0.30 g.	ascorbic acid,
1.00 g.	hydroxyethyl cellulose, high viscosity,
5.00 g.	Sodium salt of lauryl alcohol—diglycolether-sulphate (28% aqueous solution)
10.00 g.	Ammonia 22%
82.25 g.	Water
100.00 g.	

50 g. of the above hair colouring medium is mixed shortly before use with 50 ml. of hydrogen peroxide solution (6%) and the mixture is then applied to white human hair. After a period of action of 30 minutes at about 40°C, the hair is rinsed with water and dried. The hair has been dyed a deep blue-black colour.

Example 2—Hair colouring medium in gel form.

0.5 g.	2,6-di-(β-hydroxyethyloxy)-3,5-diaminopyridine dichloride
0.5 g.	2,5-diaminotoluene sulphate
0.3 g.	ascorbic acid
1.0 g.	hydroxyethylcellulose, high viscosity
5.0 g.	lauryl alcohol-diglycolether sulphate, sodium salt (28% aqueous solution)
10.0 g.	ammonia 22%
82.7 g.	Water
100.0 g.	

50 g. of the above hair colouring medium is mixed shortly before use with 50 ml. of hydrogen peroxide solution (6%) and the mixture is then applied to white human hair. After a period of action of 30 minutes at about 40°C, the hair is rinsed with water and dried. The hair has been dyed a deep blue colour.

Example 3—Hair colouring medium in gel form.

0.08 g.	3,5-diamino-2,6-diamethoxypyridine-dihydrochloride
0.30 g.	1,4-diaminobenzene
0.25 g.	resorcinol
0.30 g.	ascorbic acid
15.00 g.	oleic acid
7.00 g.	isopropanol
10.00 g.	ammonia 22%
67.07 g.	Water
100.00 g.	

Before use, 50 g. of this hair colouring medium is mixed with 50 ml. of hydrogen peroxide solution (6%) and the mixture is allowed to act for 30 minutes at 40°C on white human hair. Afterwards rinsing with water and drying is carried out. The hair has received a natural middle pale blonde colouring.

Example 4—Hair colouring medium in cream form.

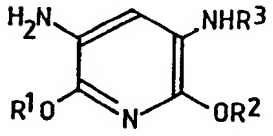
0.60 g.	3,5-diamino-2,6-dimethoxypyridine dihydrochloride
0.30 g.	4-aminophenol
0.30 g.	sodium sulphite, anhydrous
3.50 g.	lauryl alcohol-diglycol ether sulphate, sodium salt (28% aqueous solution)
15.00 g.	cetyl alcohol
3.00 g.	ammonia 22%
77.30 g.	Water
100.00 g.	

Shortly before use, this hair colouring medium is mixed with 50 g. of hydrogen peroxide solution (6%) and the mixture then applied to white human hair. After acting for 30 minutes at 40°C rinsing with water and then with a dilute citric acid solution, and then finally drying are carried out. The hair is dyed with a fashionable gold-orange tone.

All the percentages given in the preceding application represent percentages by weight.

Claims

Medium for the oxidative colouring of hair based on a developer substance—coupler substance combination and, optionally, other conventional colouring components and additives, characterised in that it contains as coupler substance, at least one 3,5-diaminopyridine derivative of the general formula I.



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wherein R^1 and R^2 independently mean CH_3, C_2H_5 or C_2H_4OH and R^3 represents hydrogen, C_1 to C_4-alkyl or C_1 to C_4 hydroxyalkyl, possibly in the form physiologically-acceptable salts.

2. Medium according to Claim 1, characterised in that it contains the coupler substance of the general formula I in a quantity from about 0.01 to 3.0 weight %, preferably 0.1 to 2.0 weight %.

3. Medium according to Claim 1 and Claim 2, characterised in that it contains as the coupler substance 3,5-diamino-2,6-dimethoxypyridine.

4. Medium according to Claims 1 to 3, characterised in that it additionally contains a known coupler substance, which is selected from resorcinol, 4-chlorresorcinol, 2-methylresorcinol, 2-amino-4-(β-hydroxyethylamino)-anisol, 2,4-diaminophenylethanol, 2,4-diaminophenoxyethanol, 2,4-diaminoanisol, 2,4-diaminophenol, 1,5-dihydroxytetralin, m-aminophenol, 3-amino-2-methylphenol, 3-amino-6-methylphenol, 4-hydroxy-1, 2-methylendioxybenzene and 4-amino-1,2-methylendioxybenzene.

5. Medium according to Claims 1 to 4, characterised in that the developer substance is selected from 1,4-diaminobenzene, 2,5-diaminotoluene, 2,5-diaminoanisol, 2,5-diaminobenzylalcohol 3-methyl-4-aminophenol and 4-aminophenol.

6. Medium according to Claims 1 to 5, characterised in that the total quantity of coupler substance—developer substance combination amounts to 0.1 to 5.0 weight %, preferably 0.5 to 3.0 weight %.

7. Medium according to Claims 1 to 6, characterised in that it contains a colouring component which is selected from 6-amino-2-methylphenol, 6-amino-3-methylphenol, 6-amino-3-ethoxyphenol, Diamond Fuchsin (C.I. 42 510), Leather Ruby HF (C.I. 42 520), 2-nitro-1,4-diaminobenzene, 2-amino-4-nitrophenol, 2-amino-5-nitrophenol, Acid Brown 4 (C.I. 14 805), Acid Blue 135 (C.I. 13 385), Disperse Red 15 (C.I. 60 710), Disperse Violet 1 (C.I. 61 100), 1,4,5,8-tetraaminoanthraquinone and 1,4-diaminoanthraquinone.

8. Medium according to Claims 1 to 7 characterised in that it additionally contains antioxidant, preferably ascorbic acid or sodium sulphite.

9. Medium according to Claims 1 to 8 characterised in that it contains a conventional additive, which is selected from water, lower aliphatic alcohols, fatty alcohol sulphates, alkyl sulphonates, alkylbenzene sulphonates, alkyl trimethylammonium salts, alkyl betains, oxyethylated fatty alcohols, oxyethylated nonylphenols, fatty acid alkanolamides, oxyethylated fatty acid esters, higher fatty alcohols, starches, cellulose derivatives, vaseline, paraffin oil, fatty acids, lanolin derivatives, cholesterol, pantothenic acid, betain, sodium hydroxide, potassium hydroxide, ammonia monoethanolamine, and triethanolamine.

10. Medium according to Claims 1 to 9, characterised in that it has a pH value of 8.0 to 11.5.

11. Process for the oxidative colouring of hair, characterised in that a hair colouring medium according to Claims 1 to 10 is applied to the hair after application of an oxidative medium, especially hydrogen peroxide, and is allowed to act for about 10 to 45 minutes at a temperature of 15 to 50°C, the hair then being rinsed, optionally washed and further rinsed, and then dried.

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